

Assessment of Pb Enrichment and Depletion in Selected Contaminated Arable Soils of Nigeria Using Calcium as a Reference Element

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Received August 16, 2013; Revised December 25, 2013; Accepted January 20, 2014

Abstract Lead (Pb) concentration was assessed of the arable soils in the vicinity of mining and dumping sites in Nigeria. Its contents in the arable soils assayed by means of atomic absorption spectrophotometry, (AAS) ranged from 6.8 – 47.8 mg/kg. The enrichment factor (EF) calculated by using calcium as a reference element fell within a range of 5.6 – 36.9. The mean values of the enrichment factor of 18.5 classified the soil as significantly contaminated with lead. Anthropogenic activities contribute significantly to the elevated level of lead in the studied areas. This poses serious debilitating effects on the agro – ecosystems, since lead has no known essential functions in plants metabolism.

Keywords: *Zamfara, arable soils, anthropogenic activities, lead, enrichment, depletion, enrichment factor*

Cite This Article: Uduma Anya Uduma, and W. L. O. Jimoh, “Assessment of Pb Enrichment and Depletion in Selected Contaminated Arable Soils of Nigeria Using Calcium as a Reference Element.” *World Journal of Agricultural Research*, vol. 2, no. 1 (2014): 5-11. doi: 10.12691/wjar-2-1-2.

1. Introduction

This research was informed by the Zamfara state (one of the studied areas) incessant acute lead poisoning epidemic. A series of lead poisoning, in Zamfara State, Northwest Nigeria lead to the deaths of at least 163 people between March and June, 2010, including 111 children, under the age of five years. Since the lead poisoning crisis was reported, it has been estimated that at least 10,000 people of which 2,000 children under 5 years of age are in acute danger of death (Reuters, 2010).

The efficiency of lead absorption from the gastrointestinal track is greater in children than in adults; and nutritional deficiencies of iron or calcium, which are prevalent in children, may facilitate lead absorption and exacerbate the toxic effects of lead (AAP, 1987). Lead is a cumulative general poison, infants, children up to 5 years of age, the fetus and pregnant women being the most susceptible to adverse health effects. Its effects on the central nervous system can be particularly serious (Ritz et al., 1988).

Research on young primates has demonstrated that exposure to lead results in significant behavioral and cognitive deficits, examples, impairment of activity, attention, adaptability, learning ability and memory, as well as increased distractibility (Rice and Karpinski, 1988).

An annual immunization program in Zamfara state, led to the discovery of a high number of childhood mortality and morbidity in Yargalma and Dareta villages, where lead is prevalent. It was thought by the villagers that all the children had contracted malaria. An investigation, by

Medecins Sans Frontie, (MSF), (Doctors without Borders), WHO and CDC (USA, Canada and Nigeria), found unusually high levels of lead in the children’s blood during tests. Studies have shown a strong positive correlation between Blood – Lead (PbB) levels in humans (UNEP, 2011, ATSDR, 1992). The UNEP conducted field research within the home environment of the local miners in September and October, 2010, and found that some well water in the villages contained 10 times the recommended limit of lead, the soil had as much as 150 times the limit of lead and air samples contained as much as 500 times the acceptable limits (UNEP, 2011).

There is increase and domestication of mining activities which is the mainstay of the local economy, in many villages in Zamfara State within the last years, with greater involvement of women and children processing lead contaminated gold ore in their home environment, including the use of cooking utensils for mining activities. Mining activities have potentially impacted negatively on public health, environmental safety and sustainable agriculture in Zamfara State. Indeed, Zamfara state is known for being the site of the worst lead poisoning outbreak in modern history, which is an ongoing crisis (UNEP, 2011). Acute lead toxicity renders the soil unsuitable for plant growth and destroys the biodiversity (Ghosh and Singh, 2005).

This study therefore, is aimed at the assessment of lead enrichment and depletion of the arable soils in the agro ecosystem of these areas. This is so because, healthy soil is essential for human health because what is in the soil affects the health, safety and quality of the food we eat that is derived from the soil (Nyle and Ray, 1999).

Lead is the commonest of the heavy elements, accounting for 13 mg/kg of the earth's crust. Industrialization, urbanization, mining, dumping and many other anthropogenic activities have resulted in the redistribution of lead from the earth's crust to the soil and to the environment (WHO, 1999). Soils with lead levels above 10 ppm average are primarily the results of lead contamination (Duggan, 1980).

Lead forms various complexes with soil components, and only a small fraction of the lead present as these complexes in the soil solution are phytoavailable (Holmgren et al., 1993). Despite its lack of essential function in plants, lead is absorbed by them mainly through the roots from soils solution and thereby may enter the human food chain (Rolfe et al., 1977). The absorption of lead by roots occurs via the apoplastic pathway or through Ca^{2+} permeable channels (Holmgren, 1993). The behavior of lead in soil and uptake by plants is controlled by its speciation and by the soil pH, soil particle size, cation-exchange capacity, root surface area, root exudation and degree of mycorrhizal transpiration (EPA, 1990). After uptake, lead primarily accumulates in root cells, because of the blockage by casparian strips within the endodermis. Lead is also trapped by the negative charges that exist on roots cell walls (Rolfe et al., 1977). Excessive lead accumulation in plant tissue impairs various morphological, physiological and biochemical functions in plants, either directly or indirectly, and induces a range of deleterious effects. It causes phytotoxicity by changing cell membrane permeability, by reacting with active groups of different enzymes involved in plant metabolism and by reacting with the phosphate groups of ADP or ATP and by replacing essential ions (Rolfe et al., 1977).

Lead toxicity causes inhibition of ATP production, lipid peroxidation and DNA damage by over production of Reactive Oxygen Species (ROS). In addition, lead strongly inhibits seed germination, root elongation, seedling development, plant growth, transpiration, Chlorophyll production and water and protein content (Holmgren et al., 1993). The negative impact of lead on plant vegetative growth mainly result from the following factors: distortion of Chloroplast ultrastructure, obstructed electron transport, inhibition of Calvin cycle enzymes, impaired uptake of essential elements such as Mg and Fe, and induced deficiency of CO_2 resulting from stomatal closure (Rolfe et al., 1977). Under lead stress, plants possess several defense strategies to cope with lead toxicity. Such strategies include reduced uptake into the cell, sequestration of lead into vacuoles by the formation of complexes, binding of lead by phytochelatin, glutathione and amino – acids and synthesis of osmolytes. In addition, activation of various antioxidants to combat increased production of lead – induced ROS constitute a secondary defense system (Holmgren et al., 1993).

Generally, lead can adversely affect ecosystems by wiping out the populations of micro – organisms at soil lead concentrations of 1000 parts per million (ppm) or more, slowing the rate of decomposition of matter (UNEP, 1991). Populations of plants, micro organisms and invertebrates may be affected by lead concentration of 500 to 1000 ppm, allowing more lead – tolerant population of the same or different species to take their place. This will change the type of ecosystem present (UNEP, 1991).

Although, many metals are essential, all metals are toxic at higher concentration, because they cause oxidative stress by formation of free radicals. Other heavy metals such as: lead, Mercury, Plutonium and Cadmium are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals / plants can cause serious illness even death. Another reason why metals may be toxic is that they can replace essential metals in pigments or enzymes disrupting their functions. Thus, metals render the soil unsuitable for plant growth and destroy the biodiversity (Ghosh and Singh, 2005).

The behavior of a given element in soil (i.e., the determination of its accumulation or leaching) may be established by comparing concentrations of a trace element with a reference element (Kabata – Pendias and Pendias, 1999). The result obtained is described as an enrichment factor (EF), and the equation used to calculate it is as follows:

$$EF = \frac{C_n / C_{ref}}{B_n / B_{ref}}$$

In which C_n is concentration of the examined element in the soil, C_{ref} is concentration of the examined element in the Earth's Crust. B_n is the concentration of the reference element in the soil, and B_{ref} is the concentration of the reference element in the Earth's Crust.

A reference element is "Conservative" (i.e., the one that content in samples originates almost exclusively from the Earth's Crust. The most common reference elements in the literature are aluminum (Al), Zirconium (Zr), iron (Fe), Scandium (sc) and, Iron (Fe), Scandium (Sc) and Titanium Ti (Blaser et al., 2000; Reimann and De Carital, 2000, Schiff and Weishberg 1999; Schrop et al., 1990, although there are also attempts at using other elements (e.g., Manganese (Mn) (Loska et al., 1979), Chromium (CR) (McMurty et al., 1995), and Lithium (Li) Loring, 1990).

Generally, the enrichment factor is used to assess soil contamination (enrichment), and its interpretation is as follows:

- EF < 2 – depletion to minimal enrichment
 - EF 2 < 5 – Moderate enrichment
 - EF 5 < 20 – Significant enrichment
 - EF 20 < 40 – very high enrichment
 - EF > 40 – extremely high enrichment
- (Sutherland, 2000).

Enrichment factor can also be used to evaluate element depletion in soil (Blaser et al., 2000). All EF values less than one may indicate that leaching and consumption of an element take precedence over its accumulation in soil.

The samples tested were collected from dumping sites in the vicinity of meaning and dumping sites in North – West, North – Central and South – East geopolitical zones of Nigeria.

The results were expected to explain which process, accumulation, or leaching is dominant in the area. The research also attempted to analyze the relationship between enrichment and depletion of the surface layer of soil and parameters such as soil pH and humus contents.

2. Materials and Methods

2.1. Location of the Research

The study areas are within Latitude 40 and 140 North and Longitude 30 and 150 East, Nigeria. These include:

1. Yargalma farming soil, near local gold ore mining site in Bukkuyum, Zamfara State, North West, Nigeria.
2. Dareta arable soil, near gold / lead ores mining site in Anka, Zamfara State, North West, Nigeria.
3. Itakpe farming soil, near iron ore mining site Okene, Kogi state, North Central, Nigeria.
4. Ray Field Resort farming soil near tin ore mining site in Jos South, Plateau State, North Central, Nigeria.
5. Udi farming soil, near coal mining site in Enugu East, Enugu State, South East Nigeria.
6. Chalawa arable soil in the vicinity of tannery waste dumping site in Kumbotso, Kano state, North West, Nigeria.
7. Court Road farming soil, near general dumping site in Kumbotso, Kano State, North West, Nigeria.

The dominant formations in the areas are carboniferous deposits with layers from the Tertiary and Quaternary periods. The predominant types of soils in the study areas are arenosols and ultisols. In small areas histosols occur.

The study areas are agricultural, industrial and mining communities. The farmland covers over 65% of the study areas. The farming activity in the study areas deals mainly with crop growing such as yam, beans, cassava, maize, pepper, Okra, leafy, vegetables, Cocoyam, rice, millet, guinea corn, tomatoes, carrot, lettuce and onions. The areas are dominated by extensive agriculture, industrial and mining activities.

2.2. Sample Collection and Analytical Procedure

The surface soil layer to a depth of 0 – 20 cm (ploughing layer) was sampled with a sharp edge plastic spatula and directly transferred the soil sample into labeled polyethylene homogenization container, and mixed thoroughly to obtain a homogenous sample representative of the entire sampling interval. Each sample from equi – spaced sample station was a composite of 30 sub – samples from a distance of 20 meters per a sub – sample. When compositing was completed, the labeled homogenization polyethylene bags were closed tightly and returned same to the laboratory for pre treatment and analysis (Mason, 1983, Barth and Mason, 1984).

The farming soil samples were air dried under laboratory conditions for two weeks, ground, sieved through a 2 – mm polyethylene sieve and dried to constant mass in an oven at 75°C, and kept in desiccators for further analysis.

0.25 g of the oven dried soil samples were weighed into platinum crucibles. The digestions were conducted with a mixture of 3 cm³ of conc. HNO₃, 2. cm³ of conc. HF and 1 cm³ of 40% H₂O₂ solution.

The mixture was digested on a sand bath at a temperature of 200 – 230°C and the acids were evaporated to dryness. After the soil had been digested and the acids evaporated, 30 cm³ of 0.25 MHNO₃ was added, warmed for 10 minutes and transferred and filtered into 50 cm³ plastic containers and filled to volume with the 0.25 MHNO₂ solution. The digested soil samples, the reagent blank and standard solutions were analyzed using Atomic

absorption, spectrometer, model BULK Scientific UPG 210.

The lead content was calculated by using the straight line equation from the calibration curve plotted.

Soil pH was measured potentiometrically in 1 MKCL with a soil / extractant ratio of 1:5 in three replicates per sample. The organic carbon was determined by Tiurin method. It was oxidized to Carbon dioxide with potassium dichromate in the presence of conc. Sulphuric acid. The unreacted potassium dichromate was titrated with ammonium iron (II) sulphate. Considering that the average content of carbon in soil organic matter was equal to 58%, the conversion factor 1.724 was used to calculate the percentage of organic matter from the content of organic carbon.

When the enrichment factor was calculated, calcium was used as a reference element. Calcium is one of the main components of the earths crust and its concentration in soil is connected mainly with the matrix. Mining interference factor (MIF) for calcium (i.e., total tonnage mined annually / total tonnage upper 2km of crust x 100 is 2.5 x 10⁻⁹ (Reiman and De Carital, 2,000) and is similar to the value for rubidium (Rb) and higher than MIF for aluminum (Al) and Zirconium (Zr), which are used as reference elements most often.

When the enrichment factor was calculated C_{ref} and B_{ref} denoted Pb and Ca concentrations in the earth's crust of 10 mg/kg and 30,000 mg/kg, respectively (Taylor and McLennan, 1995).

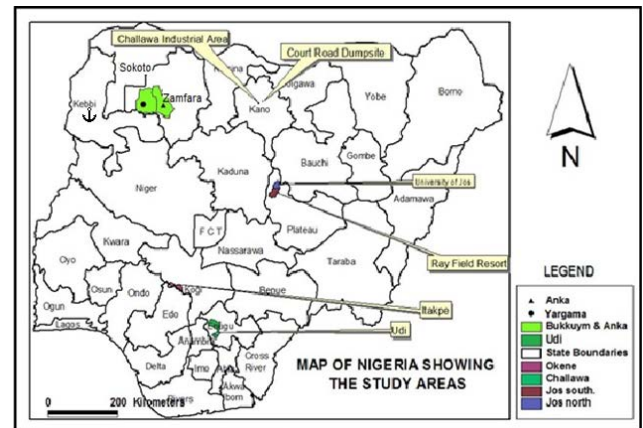


Figure 1. Map of Nigeria Showing the Study Areas

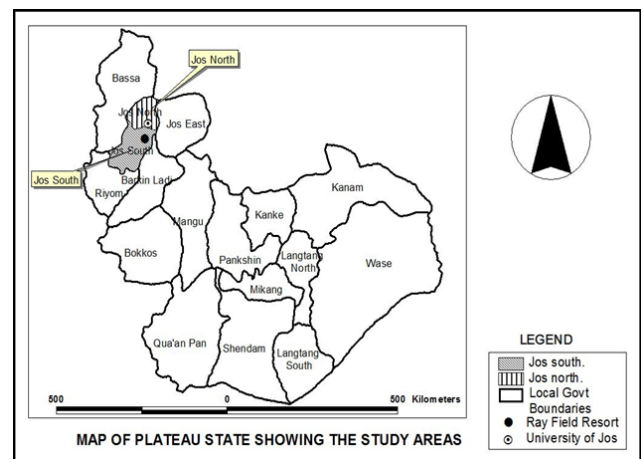


Figure 2. Map of Plateau State Showing the Study Areas

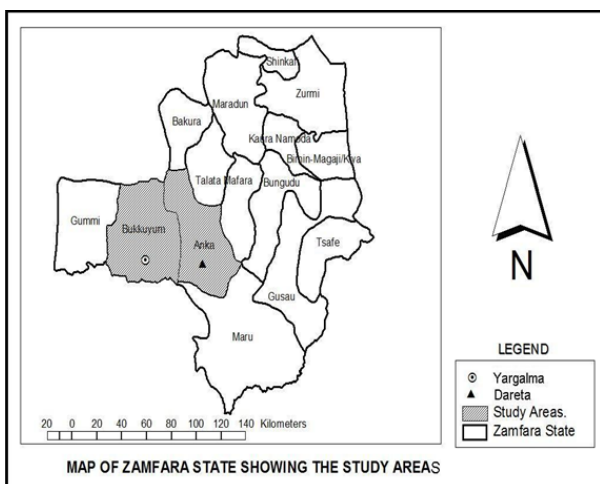


Figure 3. Map of Enugu State Showing the Study

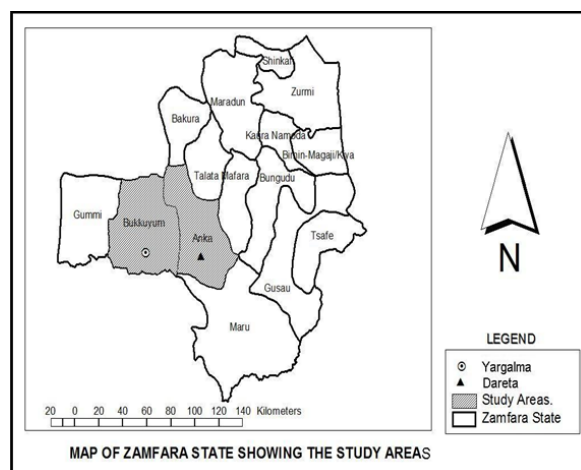


Figure 5. Map of Zamfara State Showing the Study Areas

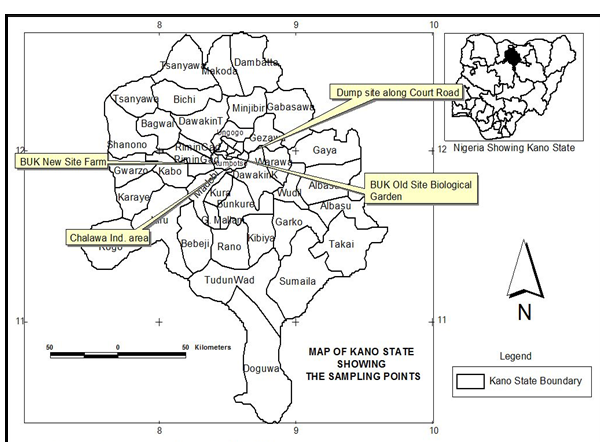


Figure 4. Map of Kano State Showing the Sampling Points

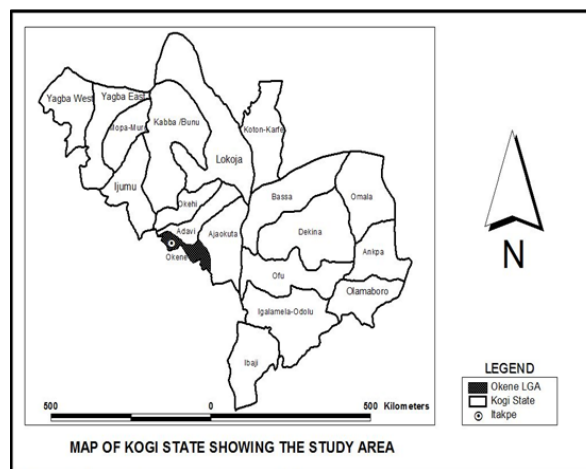


Figure 6. Map of Kogi State Showing the Study Area

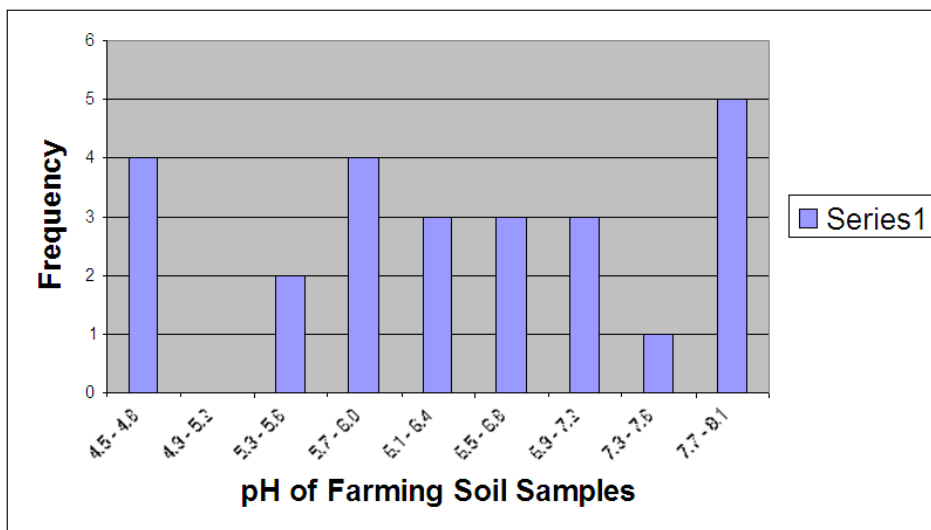


Figure 7. Distribution Pattern for pH in Farming Soil Samples

3. Results

The studied areas include Figure 1 – Figure 6. The pH of the soils (Figure 7) tested ranged from 4.1 – 8.1, indicating acidic, neutral and slightly alkaline. Humus content (Figure 8) ranged from 0.6%-4.6%. Lead (Pb) distribution skewed towards high frequently of low concentrations (Figure 9). It had a wide range of 6.8 – 47.8 mg/kg, the highest number of value being found in

47 – 51 / mg/kg range. Lead concentrations increased considerably with increasing humus content and vice versa. An increase in pH also affected significantly lead increase. The enrichment factors for the soil samples ranged over 7.7 – 36.9, indicating significant to extremely high enrichment. The mean enrichment factor of 18.5 classified the soil as significantly contaminated (Figure 10). There was no lead depletion in all soil samples assessed.

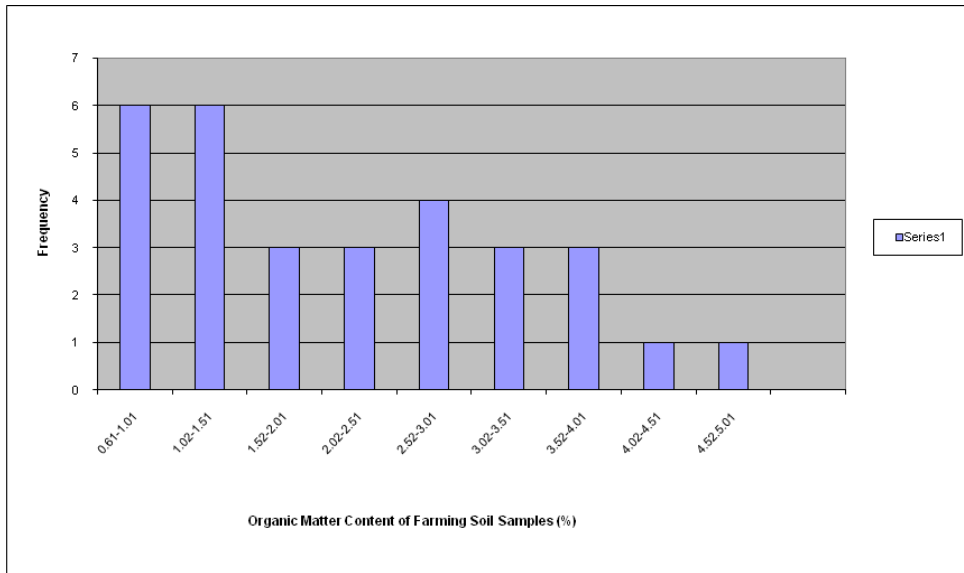


Figure 8. Distribution Pattern for organic matter in Farming Soil Samples

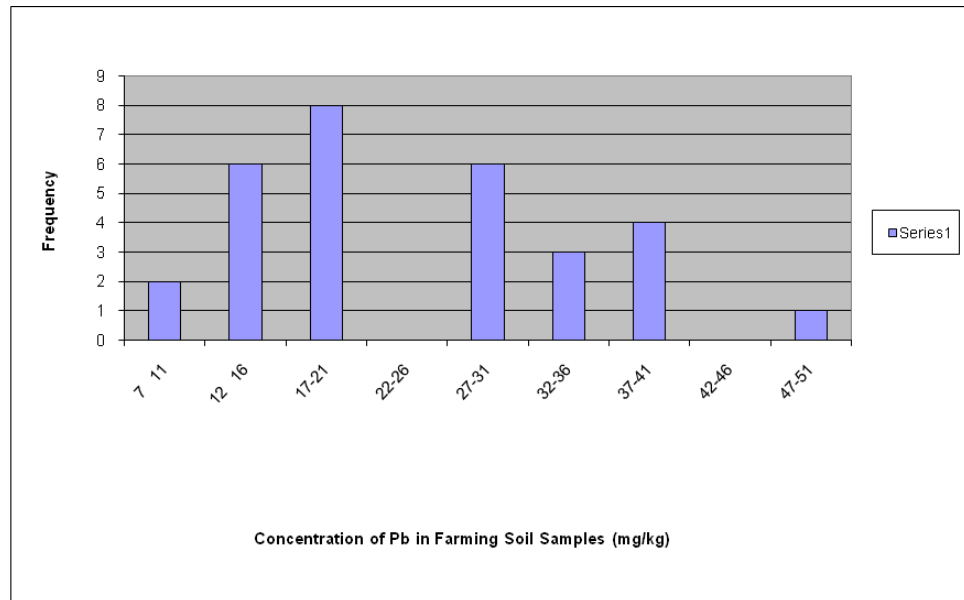


Figure 9. Frequency Distribution Pattern for Concentration of Pb in Farming Soil Samples

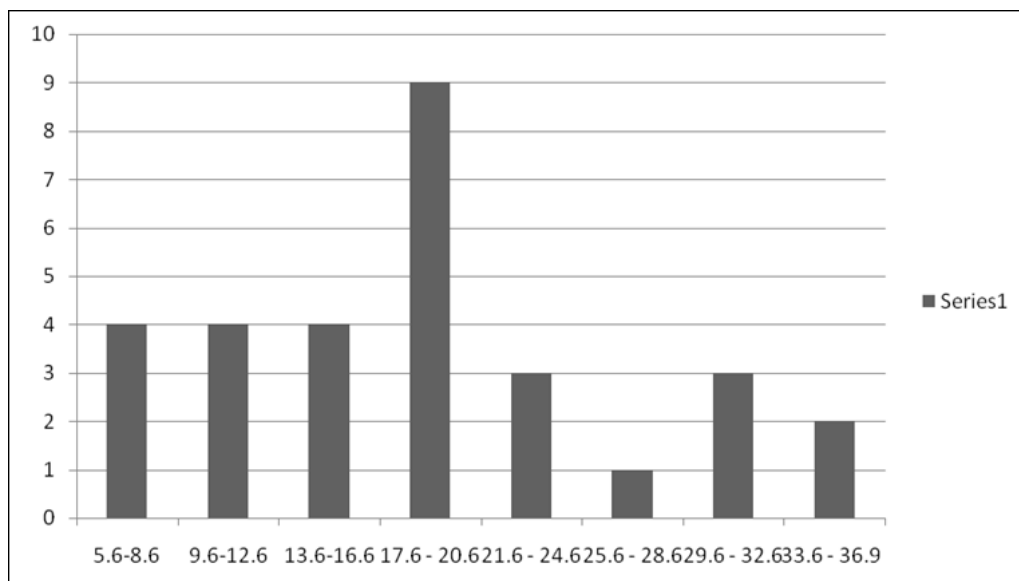


Figure 10. Frequency Distribution Pattern for Enrichment Factor of Pb in Farming, Soil Samples, using Ca as a Reference Element (Enrichment Factor (EF) of Pb in farming Soil Samples)

4. Discussion

The enrichment factors obtained pointed to significant to extremely high enrichment. The mean enrichment factor of 8.5 classified the soil as significantly contaminated with lead. This poses serious debilitating consequences on the agro – ecosystems, since lead has no known essential functions in plants. The accumulation of lead, in these study areas are essentially due to anthropogenic influence. Most of the farmers make extensive use of fertilizers, cow dung's and tannery sludge as soil amendment materials. Accumulation of lead in soils takes place in the surface layers using organic matter (Kabata-Pendias and Pendias, 1999), which is composed of simple organic compounds and humus (i.e., large – molecular, dark – colored organic bonds). Humus, like simple organic compounds, readily accumulates metals, including lead. The soils analyzed showed a distinct increase in lead concentrations with increasing humus.

An increase in soil pH, on the other hand, results in an increase in enrichment factor. Thus, the increase in pH affects greatly lead binding in soil and hinders its leaching. Humus content had a smaller effect on soil enrichment and depletion than pH.

Nigeria is one of the countries in West Africa most exposed to desert dust because of its proximity to the main emission source area and its location with regard to the dominant winds (Rutherford et al., 1999). Studies have shown that harmattan dust which deposits on vegetation and farmland contains varying degrees of metal concentrations including lead (Sunnun et al., 2008). Wastes such as lead acid battery containers, soldier, alloys, cable sheathing, pigments, rust inhibitors, glazes and plastic stabilizers are known to contain high concentrations of lead (WHO, 1989).

According to the Nigerian Federal Ministry of Environment (FME), there were 14 tanning industries around Challawa, one of the studied areas in Kano State by the year 2001, that discharge their liquid and solid wastes into the immediate environment (consisting of land and water bodies). Imamul Huq (1998), stated that various chemicals are used during the soaking, tanning and post tanning processing of hides and skins. The main chemicals used include sodium sulphate and basic chromium sulphate including non – ionic wetting agents, bactericides, soda ash, CaO, ammonium sulphide, ammonium chloride and enzymes. Others are sodium bisulphate, sodium chlorite, NaCl, H₂SO₄, formic acid, sodium formate, sodium bicarbonate, vegetable tanning, synthans, resins, polyurethane, dyes, fat emulsions, pigments, binders, waxes, lacquers and formaldehyde. Various types of processes and finishing solvents and auxiliaries are used as well. It has been reported that only about 20% of the large number of chemicals used in the tanning process is absorbed by leather, the rest is released as waste (UNIDO, 2005). Tanneries have been found to discharge not only Cr which is an inherent product of the tanning process but also significant amounts of Pb, Zn, Mn and Cu, have been observed at the main waste disposal points exceeding the toxic range in soils (Imamul Huq, 1998). These anthropogenic activities contribute significantly to the elevated level of lead in the studied areas.

5. Conclusion

The locations of the studied areas in the anthropogenically affected zones are characterized by lead enrichment of all the tested soils, and in all cases well exceeding even 100% (EF > 2) against matrix. The dynamics of humus content, pH, prevailing environmental conditions and anthropogenic impacts account for lead accumulation in the studied areas. This poses serious debilitating effects on the agro – ecosystems, since lead has no known essential functions in plants metabolism.

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